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The Asymmetric Cleavage of Diborane by Water.

The Structure of Diborane Dihydrate

by

Patricia Finn and William L. Jolly*

Abstract

The dihydrate and diethanolate of diborane have been prepared at -130° and their compositions have been established by stoichiometric measurements. The dihydrate is assigned the structure $BH_2(H_2O)_2^+BH_4^-$ on the basis of low-temperature infrared spectra of the deuterated and nondeuterated species. A study of the evolution of hydrogen from the reaction of diborane with a solution of HCl in a water-methanol mixture at -78° has provided further evidence for the asymmetric cleavage of diborane by water and alcohol.

Introduction

The cleavage of the bridging hydrogen bonds in diborane by a Lewis base, X, can be either symmetric, to give BH_3X, or asymmetric, to give $BH_2X_2^+$ and BH_4^-. In the reaction of ammonia with diborane, both types of cleavage have been observed.[1,2] With increasing methyl substitution in the methyl amine series, there is an increasing tendency for symmetric cleavage.[3-5] For various ethers, symmetric cleavage of the diborane molecule has been observed.[6] Young and Shore[7] have discussed some of the factors which may affect the course of these cleavage reactions; it appears that it is not yet possible to predict the course of such reactions with certainty.

In studies of the reaction of diborane with water[8] and alcohols[9] at room temperature, no intermediate cleavage products have been isolated because complete hydrolysis occurs rapidly. Davis and Gottbrath[10] were able to isolate sodium hydroborate from the reaction of diborane with aqueous sodium hydroxide at 0°, and Jolly and Schmitt[11] prepared potassium hydroborate by the reaction of diborane with powdered potassium hydroxide at -30°. These results are consistent with asymmetric cleavage of diborane and prompted a further study of this type reaction. This paper describes the preparation and characterization of the initial diborane-water reaction product.

Experimental

General Information.- Diborane was prepared by the addition of

KBH_4 to H_3PO_4,[12] and deuteriodiborane was prepared by the addition of

BF_3 etherate to $LiAlD_4$ in diethyl ether.[13] The purity of both compounds

was verified by vapor pressure measurements[14] and infrared spectroscopy.[15]

The $LiAlD_4$ (deuterium content 99%) was obtained from Bio-Rad Laboratories,

Richmond, California, and deuterium oxide (deuterium content 98.8%) from

International Chemical and Nuclear Corp., Chemical and Radioisotope

Division, Irvine, California. All other chemicals were of reagent grade.

Ideal gas behavior was assumed for vapors and gases when making calcula-

tions from PVT data. Low pressures of water, ethanol and methanol were

used to ensure the ideality of their vapors.

Stoichiometric Studies.- The glass reaction vessel was 20 cm long,

with three connections (one for evacuation) located at the top. Two

1/8-in. metal tubes, joined to the glass vessel with Swagelock fittings,

were suspended next to each other within the vessel with their lower

ends 1 cm from the base of the vessel. Nupro gas metering valves were

attached to the upper, outer ends of the tubes.

A hundredfold excess of diborane and either water, ethanol, or

methanol were co-condensed as an intimate solid mixture by allowing the

vapors to separately but simultaneously effuse into the vessel, which

was cooled to -196°. The inlet tubes were heated during deposition by

heating tape which was wound around the portions above the reaction

vessel. The condensed mixture was then warmed to -130° (-112° for the

methanol mixture). When the reaction was judged complete (2-3 hours for water, 1 hour for ethanol, and 2-4 hours for methanol), the excess diborane was removed by pumping. A large excess of water was condensed into the vessel and each sample was then warmed to room temperature to effect complete hydrolysis. The amount of diborane which had reacted was calculated by measuring the evolved hydrogen, which had been Toepler-pumped into a gas buret. It was assumed that each mole of diborane consumed in hydrolysis at room temperature produced six moles of hydrogen.[16]

The reaction between excess water (280 mmol) and diborane (0.20-0.25 mmol) was studied at -130° to determine the percent of diborane that reacted as a function of time. Within fifteen minutes, 86% had reacted; after two hours, 98% had reacted.

Acid Hydrolysis.- Approximately 25 ml of 0.5 M HCl in 88% by volume methanol and 12% by volume water was pipetted into a 70-ml flat-bottomed flask containing a stirring bar. The vessel was cooled to -78° using a Dry Ice-acetone bath and then was evacuated while the solution was stirred and the glass walls were heated. (The heating eliminates droplets which cause excessive decomposition.) Diborane (0.05-0.10 mmol) was introduced into the reaction vessel by momentarily opening a stopcock which connected the vessel with a chamber containing diborane gas at -130°. All unreacted diborane in the entry line was then removed by pumping. The pressure of the evolved hydrogen was measured after 40-90 seconds in a constant-volume system consisting of the reaction vessel and an adjustable manometer. The hydrogen pressures for four different runs were 0.30, 0.43, 0.64 and 0.78 cm. These pressures were corrected

for the hydrogen evolved by the hydrolysis of any H_2OBH_3 in solution using the first order rate law $a = a_0 e^{-kt}$, where $k = 2.3 \times 10^{-3}$ sec^{-1} at $-78°$ in 0.5 $\underline{M}$ HCl.[17] The corrected hydrogen pressures were 0.27, 0.39, 0.58 and 0.67 cm, respectively, assuming that the diborane reacted immediately as follows, $B_2H_6 + 3H_2O = BH_2(H_2O)_2^+ + H_2OBH_3 + H_2.$

After approximately forty minutes, the total pressure of evolved hydrogen was measured. These hydrogen pressures were 0.80, 1.11, 1.41 and 1.45 cm, respectively. The reaction vessel was then isolated from the system and warmed to room temperature to complete hydrolysis. The total pressure of evolved hydrogen was measured in the constant volume system after recooling the reaction vessel to $-78°$. The hydrogen pressures were 1.71, 2.41, 2.96 and 3.44 cm, respectively. Because the external temperature varied less than $1°$ and because care was taken to keep the level of the $-78°$ bath around the reaction vessel constant, the hydrogen pressure measurements could be used to determine the ratio of moles of hydrogen initially evolved (corrected) to moles of diborane consumed (assumed to be equal to 1/6 of the total pressure of evolved hydrogen). These ratios were: 0.97, 0.98, 1.18, and 1.18.

Infrared Measurements.- The metal low-temperature infrared-cell[18] consisted of an outer shell with CsI windows perpendicular to the optical axis and an inner part which contained the refrigerant (liquid nitrogen). From the inner part was suspended a copper block in which was mounted the CsBr plate upon which the samples were co-deposited. The inner part could be rotated relative to the outer shell during the course of the experiment, allowing the CsBr plate to be oriented normal

either to the gas inlet system or to the optical axis. The spectra were recorded on a Perkin-Elmer 221 spectrophotometer calibrated with polystyrene.

The temperature of the CsBr plate was not known accurately. The approximate temperature was estimated by measuring the vapor pressure (4 cm at -130°)[14] of the excess diborane at various times during warmup after removal of the liquid nitrogen. It took one hour of warming for reaction to occur ($\sim$ -140°), and the product remained stable during a further hour of warming ($\sim$ -100°).

Gaseous diborane and water vapor were introduced through Nupro metering valves and co-condensed on the CsBr plate cooled to -196°. In different runs, the deposition rates of diborane and water were 1-2 and 3-4 mmol/hr, respectively. The deposition time was 60-90 minutes. Longer deposition times produced a thick film of low light transmittance.

After deposition, an initial spectrum was taken at -196°. The refrigerant was then removed and the infrared cell was allowed to warm so that the diborane could vaporize and react with the porous, reactive ice. Spectra in the 3000-2000 cm^{-1} region were recorded at 5-10 minute intervals during warmup to follow the course of reaction. The vaporized, unreacted diborane was collected in a -196° trap immediately before each spectrum was run and afterwards returned to the system. Within an hour, the system was warmed to approximately -140°. The unreacted diborane (80-90%) was removed by pumping, leaving a mixture of diborane dihydrate and ice in a mole ratio of approximately 1:18. The reaction was quenched by the introduction of liquid nitrogen and a spectrum in the 4000-500 cm^{-1}

region was recorded at -196°. The refrigerant was removed, and the infrared cell was allowed to warm gradually. Spectra in the 3000-2000 cm^{-1} region were again taken at 5-10 minute intervals while continuously pumping. The peaks diminished with increasing temperature; their complete disappearance coincided with the evolution of a large amount of hydrogen (~ -100°). A final spectrum was run. Reported frequencies are accurate to ±10 cm^{-1}.

Results and Discussion

Stoichiometric Studies.- Because the diborane hydrate and diborane alcoholates decompose when the temperature is high enough to volatilize water, ethanol, or methanol, it was not possible to determine directly the amounts of these reagents that reacted with diborane when they were in excess. Therefore stoichiometric studies were possible only when using excess diborane, which is volatile even at -140°. The results of these studies are summarized in Table I. Diborane was present in at least a hundredfold excess in most of the experiments.

The diborane hydrate is relatively stable; only 3% decomposition[19] occurred in one hour at -112°. Both alcoholates, however, are much more unstable. In one hour at -130° 25% decomposition[19] of the ethanolate occurred. Decomposition is negligible at -160°; however studies were not conducted at this temperature because excess diborane cannot be removed by pumping. In the case of the diborane methanolate, 50% decomposition[19] occurred in two to four hours at -112°.
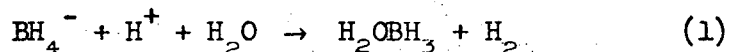
Table I

### Stoichiometric Studies of the Low-Temperature Reactions of Diborane with Water, Ethanol and Methanol

Reactant	Reactant, mmol	Diborane introduced, mmol	Diborane consumed, mmol	$\dfrac{\text{mmol } H_2O \text{ or ROH}}{\text{mmol } B_2H_6 \text{ consumed}}$
Water	0.010	3.926	0.0052	1.9
	0.017	4.050	0.0080	2.1
	0.019	3.986	0.0082	2.3
Ethanol	0.055	2.770	0.0243	2.3
	0.069	2.692	0.0307	2.2
	0.027	3.218	0.0143	1.9
	0.032	3.215	0.0150	2.1
	0.023	2.872	0.0123	1.9
	0.026	2.494	0.0150	1.7
Methanol	0.060	2.617	0.035	1.7
	0.100	3.311	0.062	1.6

For both the diborane-water and the diborane-ethanol reactions, approximately 2:1 molar ratios were found at -130° for $H_2O:B_2H_6$ and $C_2H_5OH:B_2H_6$. A lower ratio, 1.7:1, was found for the methanol-diborane system. We have no explanation for this low result, except the fact that the methanol reaction was studied at a relatively high temperature.

Hydrolysis Study.- The stepwise hydrolysis of hydroborate in acidic solution at -78° has been followed kinetically.[17] In the first step, one mole of hydroborate reacts essentially instantaneously to produce H_2OBH_3 and a mole of hydrogen.

$$BH_4^- + H^+ + H_2O \rightarrow H_2OBH_3 + H_2 \qquad (1)$$

The second step proceeds more slowly (half-time approximately five minutes at -78° in 0.5 $\underline{M}$ acid) and produces a second mole of hydrogen and $BH_2(H_2O)_2^+$.

$$H_2OBH_3 + H_2O + H^+ \rightarrow BH_2(H_2O)_2^+ + H_2 \qquad (2)$$
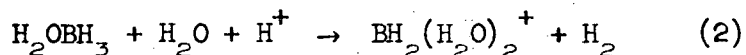
The species $BH_2(H_2O)_2^+$ is relatively stable in acidic solution (the greater the acidity, the more stable), and further hydrolysis occurs only when the temperature is increased or during prolonged standing (three to four hours).

$$BH_2(H_2O)_2^+ + H_2O \rightarrow B(OH)_3 + H^+ + 2H_2 \qquad (3)$$
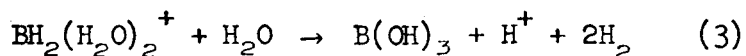
We observed the reaction of diborane with 0.5 $\underline{M}$ HCl in 88% by volume methanol and 12% by volume water. If H_2OBH_3 were the initial

product, hydrogen evolution would be gradual; in forty minutes (about eight half-times) almost two moles of hydrogen would be produced per mole of diborane. If $BH_2(H_2O)_2^+$ and BH_4^- were the initial reaction products, one mole of hydrogen per mole of diborane would be evolved instantaneously (Equation 1), and a second mole of hydrogen would be evolved during the following forty minutes (Equation 2). The latter results were actually observed. Therefore we conclude that the initial reaction products are $BH_2(H_2O)_2^+$ and BH_4^-.

Spectra.- The spectrum of the diborane-water mixture which had never been warmed above -196° consisted of the superimposed spectra of diborane and water. While warming the mixture, the diborane spectrum gradually disappeared and the product spectrum gradually appeared. After removal of the unreacted diborane from the system by pumping, the system was cooled to -196° and a clean (no unreacted diborane) spectrum of the product was obtained. When the material was again warmed, for a longer time and hence to a higher temperature, the compound gradually decomposed. The final spectrum was that of boric acid.[20] No other species were observed. In Figure 1 are presented the initial spectrum of the reactants, the spectrum of diborane dihydrate plus excess water, and the final spectrum of boric acid and water. Similar spectral studies were carried out with deuteriodiborane and deuterium oxide using the same experimental procedure, and completely analogous results were obtained. The major infrared absorption frequencies and their assignments are listed in Table II for the diborane dihydrate and in Table III for the deuterated species.

Table II

Infrared Absorption Frequencies of Diborane Dihydrate

ν, cm^{-1}	Intensity	Assignment
3200	vs	OH stretch
2750, 2720	s	BH stretch, $BH_2(H_2O)_2^+$
2420	s	BH stretch, BH_4^-
2320	s	BH stretch, BH_4^-
1605	m	OH deformation
1400	s	BO stretch
1185	s	BH deformation, BH_4^-
1155	s	BH deformation, $BH_2(H_2O)_2^+$

Table III

Infrared Absorption Frequencies of Deuterated Diborane Dihydrate

ν, cm^{-1}	Intensity	Assignment
3250	s	OH stretch (HOD impurity)
2400	vs	OD stretch
1845	s	BD stretch, $BD_2(D_2O)_2^+$
1745	m	BD stretch, BD_4^-
1700	m	BD stretch, BD_4^-
1350	vs	BO stretch
1085	s	OD deformation
885	s, shoulder	BD deformation, BD_4^-
855	s	BD deformation, BD_4^-
745	m	BD deformation, $BD_2(D_2O)_2^+$

The diborane dihydrate spectrum shows six strong bands that can be attributed to B-H bonds - four bands in the 2800-2300 cm^{-1} region (due to B-H stretching modes) and two bands in the 1200-1100 region (due to H-B-H deformation modes). Adducts of the type BH_3X show only three B-H bands - two due to B-H stretching modes and one due to H-B-H deformation.[21-23] Consequently diborane dihydrate cannot have a simple H_2OBH_3 structure. We believe that the infrared spectrum can be best interpreted in terms of the $BH_2(H_2O)_2^+BH_4^-$ structure. Salts containing cations of the type $BH_2X_2^+$ show a doublet in the 2600-2400 cm^{-1} region corresponding to B-H stretching and a single band in the 1200-1100 cm^{-1} region corresponding to H-B-H deformation.[24-26] Hydroborates typically show a peak with two shoulders[27] or three bands[28-30] in the 2400-2200 cm^{-1} region and a single band in the H-B-H deformation region.[27-30] Thus the six bands of diborane dihydrate can be accounted for by assuming the presence of $BH_2(H_2O)_2^+$ and BH_4^-.

The assignment of the high-frequency doublet in the dihydrate spectrum (with peaks at 2750 and 2720 cm^{-1}) to the $BH_2(H_2O)_2^+$ ion deserves some comment. These frequencies are about 150 cm^{-1} higher than those previously found for the B-H stretching in $BH_2X_2^+$ salts.[24-26] However, all the $BH_2X_2^+$ salts which have been previously studied have had X ligands which are relatively strong donors, usually with donor atoms less electronegative than oxygen. In $BH_2(H_2O)_2^+$, the high electronegativity of the oxygen atoms causes the boron orbitals used in the B-O bonds to have a high degree of p character. Consequently the boron orbitals used in the BH bonds have a high degree of s character, and

the BH bonds are extraordinarily strong and have a very high stretching frequency.[31] We may similarly argue that the water molecules in $BH_2(H_2O)_2^+$ are relatively poor donor molecules and that consequently the BH bonds are more nearly like those in free BH_2^+. In the latter species the boron orbitals would be sp hybrid orbitals and the B-H bonds would be stronger than those in which the boron is essentially sp^3 hybridized.

The ν_H/ν_D ratios for the BH_4^- bands have normal values: 1.39, 1.36, and 1.39, and, as expected, the B-O stretching frequency was essentially unaffected by deuteration. The ν_H/ν_D ratios for the $BH_2(H_2O)_2^+$ bands are somewhat high (1.48 and 1.55), but not unreasonable.

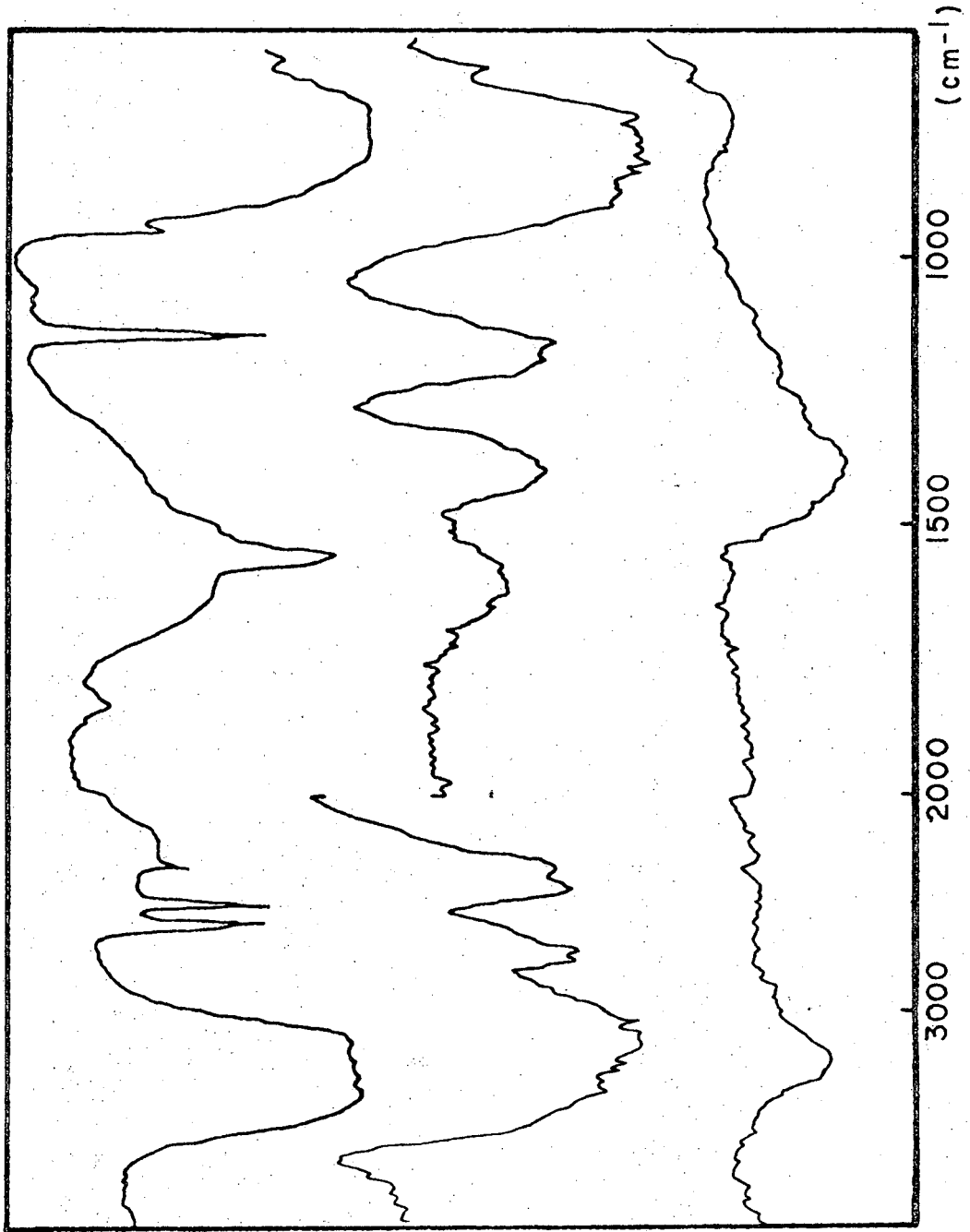## References

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Figure Caption

Figure 1. The initial spectrum of the reactants, the spectrum of

diborane dihydrate plus excess water, and the final spectrum

of boric acid and water.

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Fig. 1.